REPORT DOCUMENTATION PAGE

Form Approved
OMB No 0704-0188

1. AGENCY USE ONLY (LEAVE BLANK)	2. REPORT DATE December 1995	3. REPORT TYPE AND DATES COVERED Technical Paper

4. TITLE AND SUBTITLE

Hydrogen Peroxide for Rocket Propulsion Applications

5. FUNDING NUMBERS

C: In–House
PE:
PR: NAVY
TA: 000G

6. AUTHOR(S)

John J. Rusek

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Phillips Laboratory
OL-AC PL/RKS
10 East Saturn Blvd.
Edwards AFB CA 93524-7680

8. PERFORMING ORGANIZATION REPORT NUMBER

PL-TP-96-3015

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for Public Release; Distribution is Unlimited.

12b. DISTRIBUTION CODE

A

19961129 051

13. ABSTRACT (MAXIMUM 200 WORDS)

Traditionally, macroscopic metallic and ceramic screens have been used as catalysts for the controlled decomposition of hydrogen peroxide as applied to monopropellant thrusters, liquid rocket engines, and hybrid rocket systems. Catalyst activity depends on available catalytic surface area; metallic catalyst stability is generally degraded by catalyst oxidation. This paper will discuss new approaches to forming inexpensive, high surface area decomposition catalyst packs for flightweight applications.

The paper will specifically discuss analytical methods for the assay of hydrogen peroxide and the precise determination of inhibitor species. The synthesis, characterization, and evaluation of high surface area catalyst beds will be discussed as compared to traditional propulsion catalysts. Finally, the paper will discuss the effects of valence state and cation type of catalyst activity.

DTIC QUALITY INSPECTED 4

14. SUBJECT TERMS

hydrogen peroxide; propellant; refractometry; densitometry; inhibitor; catalyst; impregnation; calcination; gravimetry; X-ray diffraction; ICP; thermoprobe; inhibitor; valence; cation; flightweight

15. NUMBER OF PAGES

15

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	SAR

Hydrogen Peroxide for Rocket Propulsion Applications

John J. Rusek
Phillips Laboratory Propulsion Directorate
Edwards Air Force Base, California

ABSTRACT

Traditionally, macroscopic metallic and ceramic screens have been used as catalysts for the controlled decomposition of hydrogen peroxide as applied to monopropellant thrusters, liquid rocket engines, and hybrid rocket systems. Catalyst activity depends on available catalytic surface area; metallic catalyst stability is generally degraded by catalyst oxidation. This paper will discuss new approaches to forming inexpensive, high surface area decomposition catalyst packs for flightweight applications.

The paper will specifically discuss analytical methods for the assay of hydrogen peroxide and the precise determination of inhibitor species. The synthesis, characterization, and evaluation of high surface area catalyst beds will be discussed as compared to traditional propulsion catalysts. Finally, the paper will discuss the effects of valence state and cation type on catalyst activity.

INTRODUCTION

The use of hydrogen peroxide as a propellant can be traced back to Helmuth Walter and the Heinkel He176 aircraft which was first flown in 1938[1]. The 80% hydrogen peroxide was decomposed by parallel feeding liquid catalysts, generally aqueous solutions of calcium permanganate, due to its high solubility in water. The true bi-propellant arrived with the Walter 109-509 engine using C-Stoff, 30% hydrazine hydrate in methyl alcohol with 80% hydrogen peroxide[1]. The V2 ballistic missile was derived from this beginning.

The advent of the first practical heterogeneous catalyst enabled 90% hydrogen peroxide to be used as a monopropellant attitude control thruster on both the X-15 and Mercury spacecraft[2]. The catalyst used was a pack of silver plated 20 mesh brass or nickel screens. The Black Knight program in Great Britain utilized hydrogen peroxide decomposed through a silver screen pack with a kerosene based fuel as the first true bi-propellant system using peroxide in concert with a heterogeneous catalyst pack[2].

The United States Navy started using 70% hydrogen peroxide in their Mk 16 torpedo in 1955[3]. Earlier torpedoes used a homogeneous catalyst of calcium permanganate dissolved in water to react with 48% hydrogen peroxide; the new variant used a heterogeneous catalyst pack to initiate controlled decomposition of 70% hydrogen peroxide prior to mix with the kerosene-based fuel.

The current technology for the production of heterogeneous catalyst packs is the use of silver electroplated stainless steel screens, between 40 and 12 mesh, which are either activated with dilute nitric acid, or promoted via a calcined samarium oxide coating. These screens nominally have a pressure drop of 80 to 90 psig across the bed, are relatively heavy, and are readily poisoned with the typical stabilizers inherent to hydrogen peroxide. The current research is directed towards the development of a low pressure drop catalyst pack, which has a high activity, low weight and is low cost.

ANALYTICAL

REFRACTOMETRY

Refractometry allows a quick, precise and low-volume alternative to concentration determination via hygrometric methods. Approximately 40 milligrams of sample are required as compared to 110 to 170 grams for a hygrometer. A refractive index determination takes 40 seconds to perform, which makes it ideal for kinetic studies.

A Milton Roy model Abbe-3L refractometer operating at 25 °C was used to measure all refractive indices at the sodium D line (589.3 nm). The calibration of the instrument was verified with various immersion oils and a calibration standard supplied by the manufacturer (n_D=1.5113).

A set of aqueous H_2O_2 solutions was prepared by dilution of 82.1 weight percent stock material with doubly distilled water. The H_2O_2 weight fractions of these solutions were determined by standard potassium permanganate titrometric techniques. The refractive indices of the above solutions were used to generate Figure 1. These data are in excellent agreement with values quoted in the literature[4].
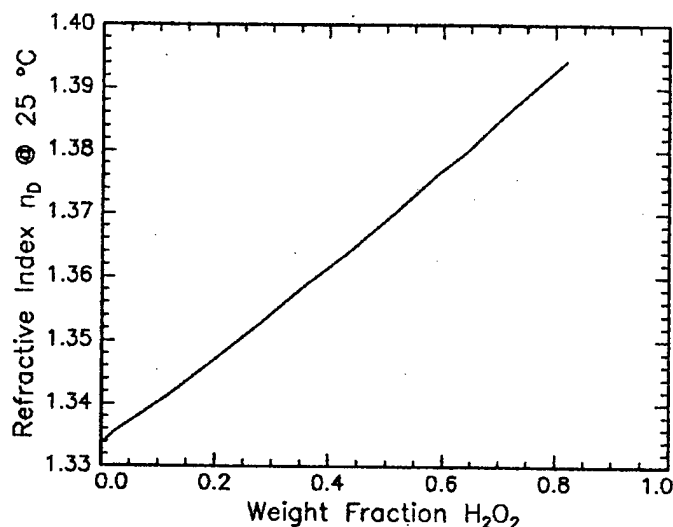

Figure 1. Graph of Refractive Index as a Function of Mass Fraction

DENSITOMETRY

Density is another easily quantifiable physical parameter which varies significantly with H_2O_2 weight fraction. The densities of aqueous solutions were measured with an Anton Paar DMA-48 ultrasonic densitometer. Although the required sample volume is approximately 0.7ml for this instrument, 5ml was used to flush the oscillator tube to insure removal of all gas bubbles.

Figure 2 shows the measured solution density, ρ, as a function of H_2O_2 weight fraction at 25 °C.
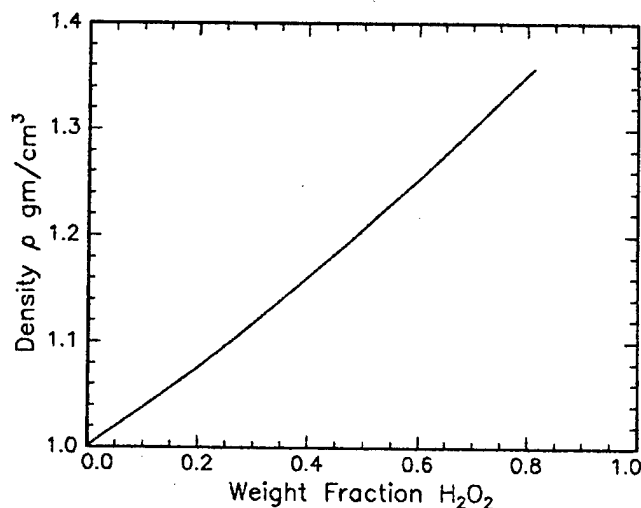

Figure 2. Graph of Density as a Function of Mass Fraction

An internal check of the above refractive index and density measurements is provided by the following relationship from molecular optics:

(1)
$$\frac{1}{\rho}\frac{n^2-1}{n^2+1} = \sum x_a \frac{P_a}{M_a}$$

where x_a is the weight fraction of liquid a of molecular refractivity P_a and molecular weight M_a. In Figure 3, equation (1) is plotted as a function of weight fraction H_2O_2 for our experimentally determined n and ρ.
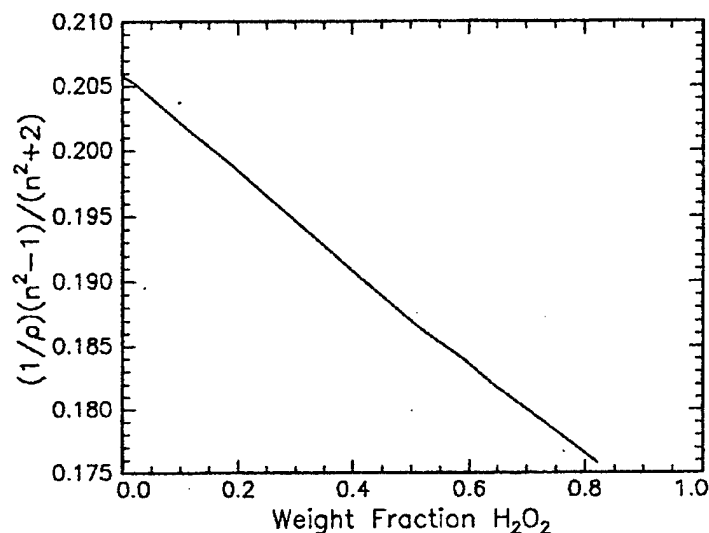

Figure 3. Graphical Representation Coupling Density and Refractive Index

INHIBITOR DETERMINATION

Of major importance to the rocket community is the identification and quantification of inhibitors added prior to shipment of the hydrogen peroxide from the manufacturers. Although the precise details of hydrogen peroxide are generally company proprietary, the industry has essentially used three general modes of inhibition. Lower concentration hydrogen peroxide uses acetaldehyde as an organic inhibitor. Medium and high concentration hydrogen peroxide are inhibited by phosphoric acid derivatives as well as sodium stannate. Technical grade hydrogen peroxides generally contain 10-30 milligrams per liter (mg/l) of sodium, tin and phosphorus. Semiconductor grade material is generally tenfold more clean, 1-3 mg/l, and rocket grade is generally tenfold again more clean, at 0.1-0.3 mg/l.

The inhibitor concentrations were quantified by using an Applied Research Laboratory model 3410 inductively coupled argon plasma (ICP). Calibration curves of line intensity versus element concentration were generated from standard solutions.

CATALYST SYNTHESIS

CATALYST BASES

The catalyst bases used in this study were all comprised of high-surface alumina or silica-alumina derived compounds. The physical shape of the particles were either oil-dropped/formed spheres or extrudate of a cylindrical geometry. The particle diameters varied from 1/16" to 1/8". Table 1 summarizes the catalyst base types and properties as obtained from the manufacturers.

Name	Type	Diameter (in.)	Composition (w/w)	Surface Area (m^2/g)	Manufacturer
3A	Extrudate	0.125	Zeolite Molecular Sieve	900	UOP
4A	Extrudate	0.125	Zeolite Molecular Sieve	900	UOP
5A	Extrudate	0.125	Zeolite Molecular Sieve	900	UOP
13X	Sphere	0.125	Zeolite Molecular Sieve	900	UOP
A305CS/S	Sphere	0.089	Al_2O_3	N/A	LaRoche
A305CS/L	Sphere	0.125	Al_2O_3	N/A	LaRoche
EAB2	Extrudate	0.063	Al_2O_3	204	UOP
SAB2	Sphere	0.063	Al_2O_3	193	UOP
SAB20	Sphere	0.113	Al_2O_3	203	UOP
SAB10	Sphere	0.063	$0.369\ SiO_2/0.631\ Al_2O_3$	340	UOP
EAB19	Extrudate	0.063	$0.419\ SiO_2/0.590\ Al_2O_3$	505	UOP
SAB30	Sphere	0.063	$0.747\ SiO_2/0.253\ Al_2O_3$	341	UOP
SAB35	Sphere	0.063	SiO_2	118	UOP

Table 1. Types and Properties of Selected High-Surface Catalyst Bases

IMPREGNATION

Initial testing of metal oxides was accomplished in concert with a literature review to narrow the field of mono-metallic catalysts studied. The results of this testing pointed to the oxides of silver, ruthenium, manganese, lead, vanadium and chromium as target species for further research.

Soluble salts of the above cations were dissolved in water to obtain solutions at a defined metals concentration of 0.96 moles per liter. Silver was obtained from silver nitrate, ruthenium from acidified ruthenium chloride, manganese from both manganous nitrate and potassium permanganate, lead from lead nitrate, vanadium from basic ammonium metavanadate and chromium from ammonium chromate.

The chosen catalyst base was dried overnight at 300°C to remove volatiles. The weighed catalyst base was then just covered with a given catalyst solution and allowed to soak for 4 hours. Generally, one-half the volume of catalyst base was used for the volume of impregnation solution. This was adjusted for variances in the catalyst base apparent bulk density. After the four hour impregnation time, the catalyst was dried in a convection oven at 80°C for 15 hours and weighed. The weight change yielded the gravimetric impregnation loading.

CALCINATION

The phase transition temperatures are widely available in the literature[5]. Table 2 outlines the decomposition temperatures of the oxide species of interest.

Calcinations were performed in a furnace by roasting in air above the defined transition temperatures for 15 hours. The calcined catalysts were allowed to cool to ambient conditions and were then weighed to yield the final gravimetric metal oxide loading.

Species	Valence	Transition Temp (°C)
Ag_2O	+1	230
Ag	0	
MnO_2	+4	535
Mn_2O_3	+3	1080
Mn_3O_4	+3/+2	
PbO_2	+4	290
Pb_2O_3	+3	370
Pb_3O_4	+3/+2	500
PbO	+2	
V_2O_5	+5	1750
VO_2	+4	
CrO_2	+4	300
Cr_2O_3	+3	

Table 2. Transition Temperatures and Valence States of Active Catalytic Promoters

CATALYST CHARACTERIZATION

GRAVIMETRY

A relatively precise assessment of what is adsorbed by the catalyst base was obtained by gravimetric analysis. The differential weight obtained through the drying and calcination processes was recorded relative to the catalyst base. This differential gave the metal oxide loading, and was recorded in weight percent.

Catalyst bases were subjected to the impregnation, drying and calcination processes using distilled water. This gave a valid blank for a given catalyst base.

Gravimetry was coupled with x-ray diffraction to yield metal loading, since the oxide composition coupled with oxide loading determines the metal loading through a gravimetric factor.

X-RAY DIFFRACTION

In lieu of absorption measurements, valence information was inferred from X-ray crystallography data gathered on a Scintag Inc. model XDS-2000 powder diffractometer system utilizing Ni filtered Cu K_α radiation. The data were peak fitted and compared to known powder diffraction patterns from an on-line JCPDS CD-ROM database.

Due to low loading of the catalyst bases, witness samples of each cation were prepared following the same thermal treatment as the catalyst. Each sample was ground to approximately 320 mesh. Long integration times were chosen to facilitate identification of minor phases (less than 0.5% by weight) and to overcome absorption (and fluorescence) problems of the Mn systems due to its proximity to Cu in atomic number.

METALS LOADING BY ICP

Weighed samples of the calcined catalyst were digested in a defined volume of either concentrated hydrochloric acid or aqua regia for 24 hours at ambient conditions. This resulted in a solution of the metal species which was suitable for ICP analysis.

BATCH ACTIVITY TESTING

The decomposition of hydrogen peroxide follows first order kinetics. The following equation defines the relationship for a first order reaction.

$$(2) \qquad -\ln Ca/Ca_0 = kt$$

where:
Ca is the batch hydrogen peroxide concentration at time t, in moles/liter,
Ca_0 is the initial batch hydrogen peroxide concentration, in moles/liter,
k is the first order rate constant, in sec^{-1},
t is the time, in sec.

By plotting $-\ln Ca/Ca_0$ as a function of time, it is possible to see if a reaction is truly first order.

The rate constant k has been defined for a homogeneous system. It is preferable to define it on a catalyst specific basis. For this study, a catalyst weight basis was chosen. The new specific rate constant, k', was defined as the experimentally determined rate constant divided by the catalytic metal loading, in grams.

The batch reactor used was a 50 ml spherical glass flask containing 20 ml of 70% hydrogen peroxide. The solution was stirred at a defined angular velocity with a magnetic stirrer and a glass encapsulated thermocouple was inserted into the solution. At time t = 0, a precise weight of catalyst was admitted to the hydrogen peroxide solution. 40 µl aliquots were withdrawn from the batch at defined time intervals which were then analyzed by refractive index. A temperature history was also obtained for each experimental run.

By plotting $-\ln Ca/Ca_0$ versus time, and knowing the catalyst metal loading, k' was obtained for a variety of catalyst types.

THERMOPROBE TESTING

The decomposition of hydrogen peroxide is exothermic; 70% hydrogen peroxide gives off 23 kilocalories per mole as its heat of reaction. For this reason, a purely isothermal activity test was difficult. A test was developed, coined the thermoprobe analogy test, in which a defined volume (20 ml) of 30% hydrogen peroxide was reacted with a known volume of catalyst (3.2 ml) in a vigorously stirred spherical reactor (100 ml). The reactor wetted surface to volume ratio is therefore constant and thermal losses can be quantified during reaction.

Thermal history was obtained for each run; peak temperature and time to peak temperature were obtained. The time to peak temperature as a function of metal loading for a given volume is a direct indicator of catalyst activity.

The thermoprobe analogy test uses a constant volumetric catalyst basis, which is of prime interest to the rocket designer.

RESULTS AND DISCUSSION

HYDROGEN PEROXIDE STUDIES

Three grades of hydrogen peroxide were analyzed which are of interest to the rocket community. Table 3 shows the concentration results via refractive index and the inhibitor loading via ICP for the three types.

All of the above grades do not meet the rocket propulsion specifications cited earlier. This is indicative of the current state of hydrogen peroxide manufacture; hydrogen peroxide is mainly used in bleaching and wastewater

remediation where inhibitor concentration is not critical. It is important to note that the FMC Semiconductor grade most closely matches the grade used on the Scout rocket, although both are off the original military specification.

%	P(mg/l)	Na(mg/l)	Sn(mg/l)	Source
63.9	0.68	2.01	0.67	FMC/SC 70
62.3	15.9	23.8	6.83	SOLVAY 70
80.8	0.75	3.84	1.33	SCOUT 90

Table 3. Comparison of Various Commercial Grades of Hydrogen Peroxide

X-RAY DIFFRACTION RESULTS

The XRD results of the witness samples are given as Table 4. The thermal decomposition products of potassium permanganate did not match any combination of known compounds listed in the JCPDS database. However, there was strong evidence that K_2MnO_4 is one phase present. Several possibilities have been proposed but at this time the exact identities of the decomposition products and therefore the oxidation states of Mn, remain uncertain.[6,7]

Starting Material	Temperature (°C)	Phase
$Mn(NO_3)_2$	210	MnO_2
	450	MnO_2
	600	Mn_2O_3
$KMnO_4$	450	Unknown
	600	Unknown
$Pb(NO_3)_2$	280	PbO
$RuCl_3$	600	RuO_2
NH_4VO_3	210	V_2O_5
	600	V_2O_5

Table 4. Summary of XRD Witness Sample Analysis

CATALYST ACTIVITY RESULTS

BATCH ACTIVITY TESTING

The batch activity test was first run on a 13x spherical molecular sieve loaded with a potassium promoted manganese oxide. Figure 4 shows a plot derived from Equation (1).
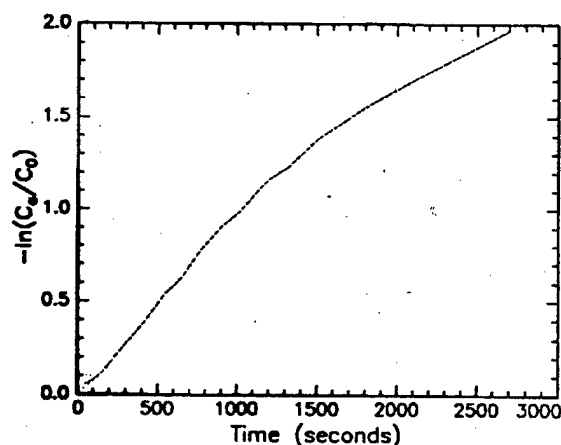
Figure 4. -ln Ca/Ca_0 as a Function of Time for the Catalyst System K/Mn_xO_y on 13X Spherical Molecular Sieves.

The first 1000 seconds of the reaction are linear. Past that point, poisoning, or a temperature effect causes a deviation from linearity. The initial slope, up to 1000 seconds, was defined as the first order rate constant, k. The rate constant was then normalized to the active catalyst metal weight, as discussed previously, to generate k'. A variety of synthesized catalysts were evaluated by the Batch Activity Test method discussed in the previous section. The results of these activity tests are shown as Table 5.

Base	Catalyst	Impregnated Loading (w%)	Calcined Loading (w%)	Rate Constant k, $10^{-6}(s^{-1})$	Specific Rate k', $10^{-3}(s^{-1}g^{-1})$	Relative Activity
A305CS/L	Ag_2O	1.10	1.18	19.3	5.38	3
A305CS/L	RuO_2	0.04	0.01	4.18	155	86
A305CS/L	MnO_2	7.27	0.14	19.4	103	57
A305CS/L	MnO_2	7.27	0.23	30.4	108	60
A305CS/L	Mn_2O_3	7.27	0.33	38.0	81	45
A305CS/L	K, Mn_XO_Y	0.15	0.09	10.9	94	52
A305CS/L	K, Mn_XO_Y	0.15	0.16	40.6	102	56
A305CS/L	PbO	1.50	1.61	8.35	1.81	1
A305CS/L	V_2O_5	0.42	0.40	8.3	9.5	5
EAB2	K, Mn_XO_Y	N/A	1.85	133	111	62
SAB2	K, Mn_XO_Y	N/A	3.68	146	176	97
SAB10	K, Mn_XO_Y	N/A	1.91	54.9	197	109
EAB19	K, Mn_XO_Y	N/A	2.61	158	74	41
SAB30	K, Mn_XO_Y	N/A	2.64	111	180	99

Table 5. Batch Activity Testing Results for Selected Catalysts and Base Using 70% Hydrogen Peroxide. Relative Activity Values are Referenced to Lead Oxide Specific Rate in All Cases.

For a given catalyst base, adsorption varies widely as seen from the impregnated loading values, column three. As stated previously, the initial impregnation solutions were all fixed at 0.96 moles per liter, yet the loaded catalyst values indicate a factor of 180 difference between the smallest loading, derived from ruthenium chloride, to the largest, derived from potassium permanganate.

The difference between the impregnated loading value and the calcined loading value indicates the degree of fugitiveness of the metal catalyst during the calcination process. The most volatile species appears to be manganese derived from manganous nitrate which shows a loss of a factor of 52 in metal concentration during

calcination. Note that there is negligible loss of manganese upon calcination if potassium permanganate is used as the impregnation salt.

Relative activity is defined with respect to the lowest rate constant catalyst studied, in this case, lead oxide. It is interesting to note that all of the manganous species show similar relative activities, in the mid to high 50's, with the exception of the trivalent oxide, Mn_2O_3. It is also important to note that the addition of a base promoter to manganese apparently does not affect the catalyst relative activity. Ruthenium oxide is seen to have a high relative activity, but the loading is quite low, almost in the noise of the analytical technique, hence, the value should be viewed with caution. A surprising result is seen in the case of silver oxide, among the least active of the catalysts. It is inferred from this that silver is an active catalyst, not silver oxide.

The effect of varying catalyst bases with a constant impregnation solution is seen as the last five entries. SAB2 adsorbed twice as much active metal catalyst than the EAB2 variant. Even with the low adsorption of SAB10, the catalyst derived from SAB10 proved to have the highest relative activity in this series of runs.

THERMOPROBE ANALOGY TESTING

Thermoprobe testing, as discussed in the previous section, was done on a number of traditional and proposed rocket propulsion catalysts and bases. The results of these thermal tests are shown as Table 6.

Base	Catalyst	Loading (w%)	Total Weight (g)	ΔT_{MAX} (°C)	Time to ΔT_{MAX} (m)
13X	K, Mn_XO_Y	1.35	1.909	73.3	4.7
SAB10	K, Mn_XO_Y	2.63	1.472	61.0	6.3
Al_2O_3	Pt	0.50	2.816	68.6	0.9
Purofil	(MnO_2)	N/A	2.063	56.2	0.6
SS Screen	Ag/SmO_2	N/A	4.314	54.6	12.9

Table 6. Results of Thermoprobe Analogy Testing of Heterogeneous Propulsion Catalysts Using 30% Hydrogen Peroxide. All Catalysts were Tested at a Constant 3.2 ml Volume

Purofil is not technically a catalyst, but a reactant. It forms manganese dioxide in contact with hydrogen peroxide. The oxide formed has a very high surface to volume ratio, as it is in the colloidal state. The main drawbacks of Purofil in propulsion applications are the downstream contamination of the rocket combustion region and its quick disappearance during the action time of the rocket; it is included for completeness.

As discussed previously, the time to attain a maximum temperature rise is a direct indicator of catalyst activity. The actual maximum temperature is
an indirect measure of activity, folded into heat loss of the batch reactor. It is seen from Table 6 that the most active species is Purofil.

Dispersed platinum on alumina is a very active catalyst, followed by the manganese loaded 13X and SAB10 variants. The least active catalyst was the samarium promoted silver screen, the conventional peroxide decomposition catalyst.

In order to further understand the effects of equivalent loading, a series of experiments were conducted varying the number of catalyst pellets for a fixed volume of hydrogen peroxide. Table 7 shows the results of this testing for four catalyst variants.

Base	Catalyst	Metals Loading (w%)	Catalyst Volume (mm)	r_{eff}(mm)	Total Batch Metals (mg)	Time to ΔT_{MAX}(m)	Activity (h^{-1})
13X	K, Mn$_X$O$_Y$	1.35	666	5.4	0.77	30.4	1.97
13X	K, Mn$_X$O$_Y$	1.35	1330	6.8	1.57	9.9	6.06
13X	K, Mn$_X$O$_Y$	1.35	2660	8.6	2.89	2.5	24.0
Al$_2$O$_3$	Pt	0.50	116	3.0	0.97	9.2	6.52
Al$_2$O$_3$	Pt	0.50	231	3.8	1.76	3.8	15.8
Al$_2$O$_3$	Pt	0.50	462	4.8	3.61	2.0	30.0
A305CS/L	MnO$_2$	0.23	293	4.1	0.79	105.0	0.57
A305CS/L	MnO$_2$	0.23	586	5.2	1.55	64.1	0.94
A305CS/L	MnO$_2$	0.23	1170	6.5	3.30	33.3	1.80
A305CS/L	K, Mn$_X$O$_Y$	0.09	293	4.1	0.29	124.2	0.48
A305CS/L	K, Mn$_X$O$_Y$	0.09	586	5.2	0.59	56.2	1.07
A305CS/L	K, Mn$_X$O$_Y$	0.09	1170	6.5	1.22	38.5	1.56

Table 7. Thermoprobe Analogy Testing Derived Parameters and Results for Supported Catalyst in 30% Hydrogen Peroxide. Activity Defined as the Inverse of the Induction Time.

Effective volume is calculated by measuring the catalyst pellets, calculating a volume per pellet and multiplying by the total number of pellets used in an experiment. The effective radius is the radius derived by assuming a sphere having that effective volume. Total batch metals is obtained by knowing the total catalyst weight and multiplying by the metals loading. Activity is defined as the inverse of the time to maximum temperature.

The 13X with potassium promoted manganese and Pt on alumina catalysts both have a relatively high surface area. This is directly reflected in their activity values. The A305CS/L base catalysts had considerably lower activity than the previous two.

Data contained in Table 7 has been plotted as Figures 5 and 6. Figure 5 shows the log of catalyst activity as a function of the log of effective radius.

One would expect a straight line with a slope of 2 if the external surface area dominated, and a slope of 3 is the total catalyst volume dominated. The curves depicted within Figure 5 are seen to approximate straight lines, within the bounds of the experiments. If anything, the 13X line exhibits a slight concavity to the left and the supported Pt catalyst exhibits a slight concavity to the right. In the extreme, this implies that the supported Pt catalyst will 'saturate' in activity with increasing radius, while the 13X catalyst will accelerate in activity with increasing radius.

As can be seen, the A305CS/L catalysts both have identical slopes of 1.73, indicating a slightly less than external surface dominating mechanism. The supported Pt catalyst shows a slope of 3.24, indicating slightly more than a volume dominating mechanism, perhaps due to some internal surface are contribution. The 13X catalyst shows the highest slope of 5.31, indicating a great contribution due to internal surface area.

Figure 6 illustrates log activity as a function of total batch metals concentration.
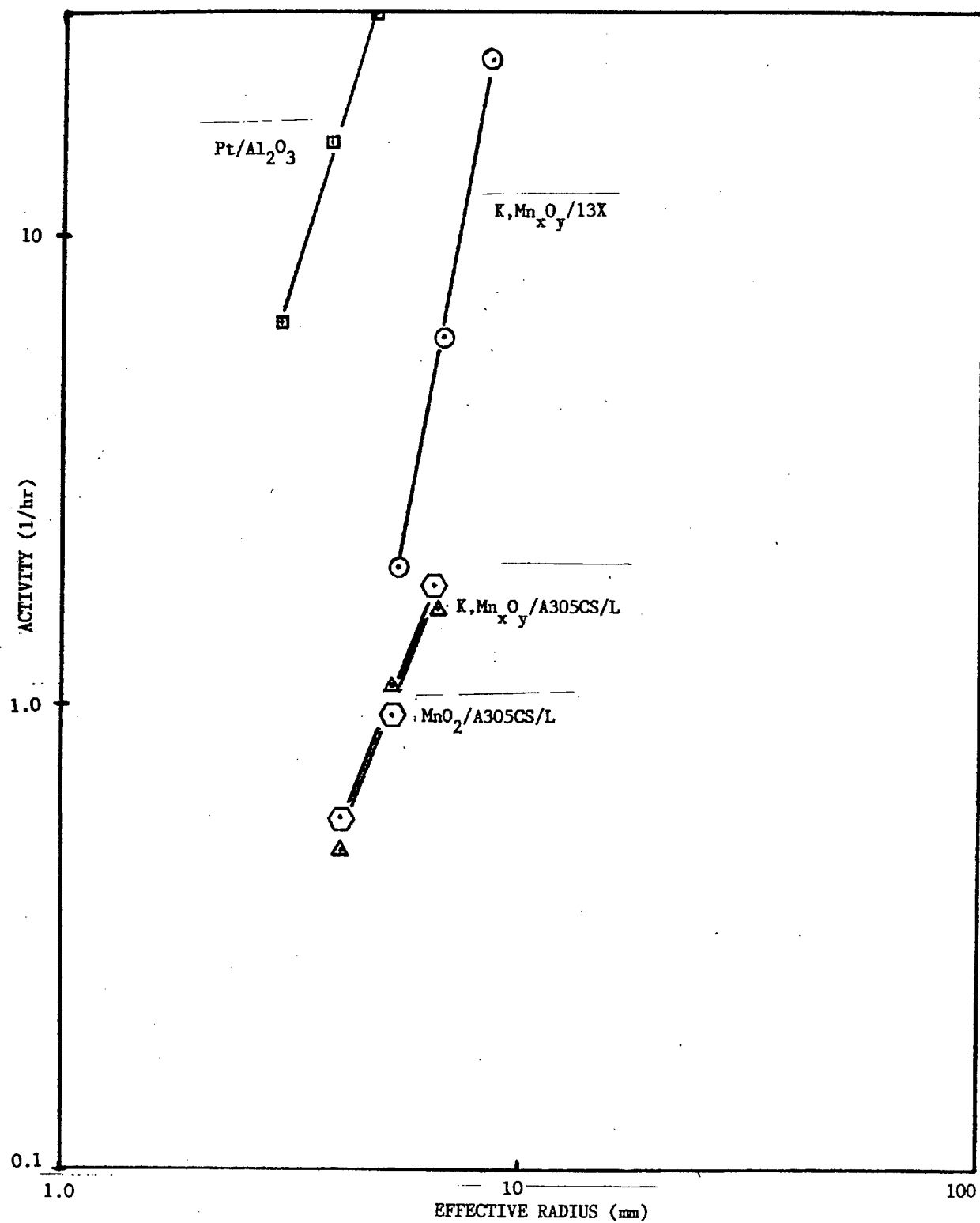
Figure 5. Log Activity as a Function of Log Effective Radius Derived From Thermoprobe Analogy Tests.
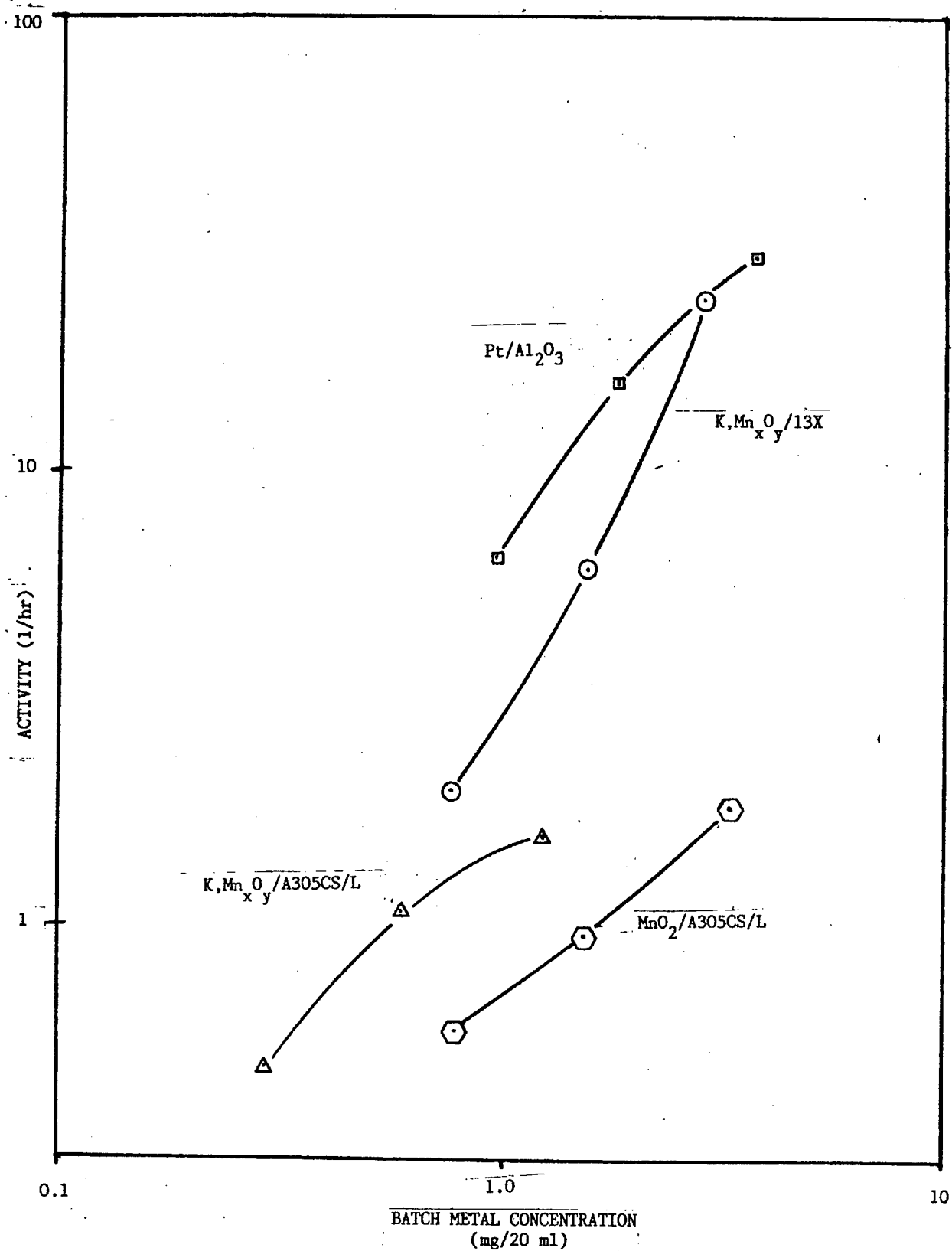
Figure 6. Log Activity as a Function of Log Batch Metals Concentration Derived From Thermoprobe Analogy Tests

As can be seen, the rate of change of activity with concentration is most noticeable with the 13X catalyst. From this graph, the crossover point occurs at 3 mg per 20 ml. Above this concentration, the manganese oxide is a better catalyst, on a high surface substrate; below this value, the platinum is superior. The method to enable this within a given catalyst volume is to increase the metals loading of the catalyst particles.

Figures 7, 8, 9 and 10 are micrographs of cleaved catalyst particles used in Table 6.

Figure 7. SEM Photomicrograph of Cleaved Catalyst Particle: A305CS/L Loaded with Manganese Dioxide

Figure 8. SEM Photomicrograph of Cleaved Catalyst Particle: A305CS/L Loaded with Potassium Promoted Manganese Oxide
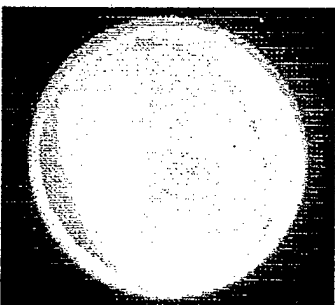

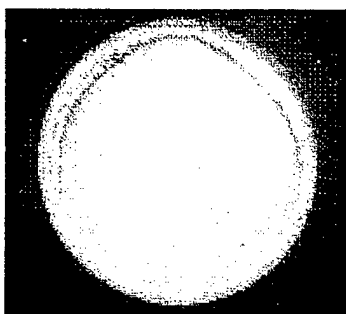Figure 9. SEM Photomicrograph of Cleaved Catalyst Particle: Platinum Loaded on Alumina

Figure 10. SEM Photomicrograph of Cleaved Catalyst Particle: 13X Molecular Sieve Loaded with Potassium Promoted Manganese Oxide

As can be seen from these photographs, the A305CS/L base shows no significant diffusion of the impregnation solution, hence the active catalytic agent, to the pellet interior. This was shown as well by the thermoprobe activity tests.

The supported platinum catalyst shows slight diffusion into the pellet, but most of the active catalyst is in the external 10% of the volume.

The 13X catalyst shows good diffusion throughout the molecular sieve. This coupled with the activity results indicates that internal surface area is important to catalyst activity.

All of the activity testing was done in the batch mode to assess catalyst activity. Another important parameter is catalyst stability, especially in a rocket motor of relatively long duration, subject to throttling or shutdown and startup cycles. To fully address catalyst stability for these applications, flow systems through a fixed catalyst bed with proper instrumentation is desired, which will be the focus of future work.

CONCLUSIONS

The following conclusions are obtained from the batch activity testing of hydrogen peroxide decomposition by heterogeneous catalysts.
1)   Relatively low-cost, low-weight catalysts have been formulated with higher activity than conventional silver screen catalysts.
2)   Refractive index is a convenient, low volume and accurate method to determine the concentration of hydrogen peroxide.
3)   High-surface catalyst bases are essential to producing highly active catalysts.
4)   Tetravalent manganese is more active than trivalent manganese as a catalytic agent.
5)   Base-promoted manganese exhibits lower weight loss during calcination than manganese alone.
6)   It appears that neutral silver is more catalytically active than silver oxide.
It is recommended that a flow reactor be used to assess catalyst stability and erosion rates at rocket firing conditions; this work is planned for next fiscal year.

ACKNOWLEDGMENTS

[1] Andrews, D., "Advantages of Hydrogen Peroxide as a Rocket Oxidant," *Journal of the British Interplanetary Society,* Vol. 43, No. 7 July 1990

[2] Sellers, J.J., Meerman, M., Paul, M., and Sweeting, M., "A Low-cost Propulsion Option for Small Satellites," *Journal of the British Interplanetary Society,* Vol. 48, No. 3 Mar 1995

[3] Wolf, S., "Hydrogen Peroxide as a Torpedo Propellant," U.S. Naval Underwater Ordnance Station Report-360, March 1963

[4] *CPIA Publication No. 394, Volume III, Unit 16,* September 1984

[5] Weast, R.C., *Handbook of Chemistry and Physics, 67 Edition,* 1986-1987

[6] Kolyshev, A.N., "On possible Structural Transformations during the Thermal Decomposition of Potassium Permanganate," *The Russian Journal of Inorganic Chemistry,* Vol. 38, No. 4, 1 April 1993, pg. 539

[7] Brown, M.E., Galwey, A.K., Mohamed, M.A., Tanaka, H., "A mechanism for the thermal decomposition of potassium permanganate crystals based on nucleation and growth," *Thermochimica Acta,* Vol. 235, No. 2, 21 April 1994, pgs. 255-270